DOCTOR OF SCIENCES

Selective growth of CdTe by molecular beam epitaxy on CdTe(211)B microseeds and Si(100) nanoseeds patterned on SiO2

Seldrum, Thomas

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University of Namur

Chapter I. Introduction

Every second, 15 TJ are consumed to provide the huge energy requirements of our modern societies, this is 700% more power than 50 years ago. The energy is mainly produced by burning fossil fuels. They account for 87% of the total production of energy. Table I-1 shows the different energy sources and the power generated by each of them [1, 2]. The proportion of each energy source is given in Figure I-1. The fossil fuels can be volatile (methane), liquid (petroleum) or solid (coal) and the generation of these products is a very long lasting process (millions of years).

Energy source	Power (TW)
Oil	5.6
Coal	3.8
Gas	3.5
Nuclear	0.9
Renewable energies	1.1

Table I-1. Worldwide energy production by energy sources in 2005.

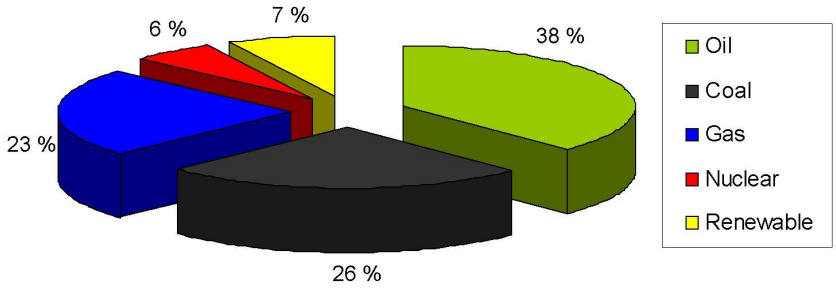

Figure I-1. Production percentage of the energy sources.

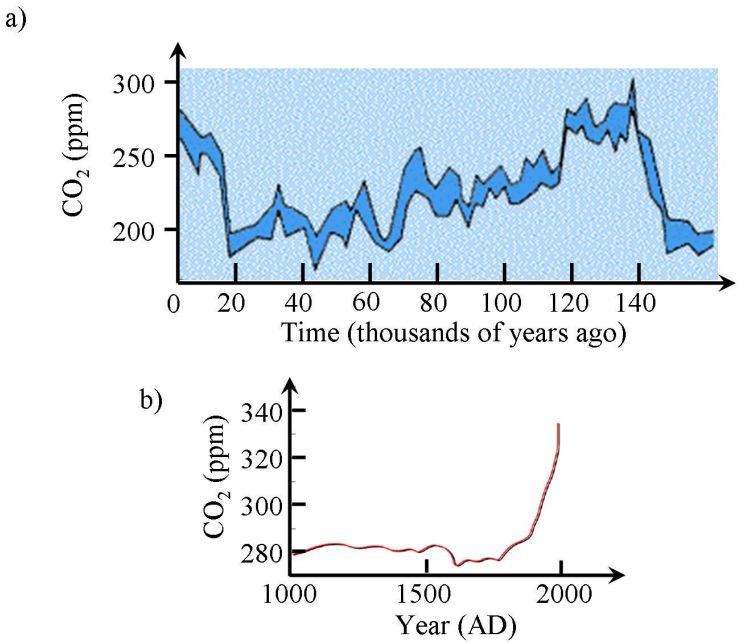

Figure I-2. CO_2 concentration in the atmosphere (in ppm) a) for one ice age cycle [3]; b) from 1000 to 2000 AD [4].

The main problem of fossil fuels is that they generate extensive pollution when they are burned to be converted into energy (heat, electricity…):

- Emission of carbon dioxide (CO_2), of which only 50% is estimated to be absorbed by natural processes. This is the primary cause of global warming: the concentration of CO_2 is correlated to the Earth's temperature and thus to the ice age cycles (Figure I-2a). Nowadays, the concentration of CO_2 in the atmosphere represents 125 % of the highest concentration ever measured. This rise is observed since the beginning of the industrial revolution in the early 1800s (Figure I-2b);
- Production of SO_2, a gas responsible for acid rains which damage the environment. SO_2 can also form airborne particles which are inhaled and remain in the lungs. These particles cause breathing diseases and premature death;
- NO_x vapors are emitted during the combustion. This gas is a precursor to the formation of ozone which inflames the lungs;
- Carbon monoxide (CO), a lethal poison when inhaled at high dose but which is also responsible for headaches and a threat for people suffering from a heart disease;
- Emission of volatile organic compounds which form ozone;
- Heavy metals (Hg, Cd, Pb, As…) are also emitted and can pollute rivers and oceans, making fish unsafe to eat and inducers of cancers.

More indirect sources of pollution should also be taken into account:

- Production of solid wastes (ash and sludge) which are disposed in surface impoundments and onsite landfills. These wastes can contaminate drinking water, leading to subsequent damage of the nervous system and vital organs of human beings. The surrounding ecosystem can also be in great danger because of these contaminations;
- Power plants are usually cooled down by water from a nearby river. The water that is released at the end of the cooling process is hotter and the induced thermal pollution can decrease the fertility and increase the heart rate of fish. Moreover, chlorine is often used to avoid the growth of algae and these toxic chemicals are discharged back into the environment;
- Coal and crude oil is transported from refineries to power plants by locomotives and tanker ships. Such transportation requires additional use of fossil fuels;
- The last pollution consists of the waste of energy: for a coal plant, the efficiency for electricity conversion from coal is only 33 %.

In addition to the pollution generated, the reserves of fossil fuels are not unlimited. Experts predict that, if the growth of our needs in energy remains constant, we will run out of oil in 2045 and coal in 2160. All these considerations lead to the consequence that we have to find alternative ways to provide the energy required for our needs.

Nuclear power plants can be a candidate. However, it is difficult to get rid of the main disadvantages of nuclear power: radioactive waste (liquid or solid) cannot be destroyed and need to be stored for thousands of years (even if only 10 grams of highly radioactive wastes are produces to provide the energy required for one person in one year); radiation leaks poison and increase the risk of cancer; the dissipation of heat in the water of the surrounding lakes and rivers used as cooling system for the reactor, causing the growth of algae and killing the marine life.

The best should be to focus on solar energy. At the present time, among the renewable energies, solar energy represents presently only 0.5 % of the total energy production in the world while the total solar power reaching the Earth's surface represents 1000 times more than what is required for our present civilization (10^{15} W). If the other main sources of renewable energies (wind and hydrothermal) are added, 87000 TW are available. Solar energy is a pollution free source of energy…except for the manufacturing of photovoltaic cells: it requires energy derived from power plants using fossil fuels. Taking into account the energy needed to purify the components of the solar cell and its manufacturing, it has been estimated that 1 kWh of energy from a solar cell generates 55 grams of global warming pollution whereas the same amount of energy from a coal-fired power plant is responsible for the emission of 1 kg of greenhouse gases [5].

Nowadays, the interest in solar cells is growing among the industrialized countries to tackle the problem of finding renewable energy.

The basic principle of a solar cell is always the same: a photon enters a semiconductor material and an electron-hole pair is created if the photon is absorbed. The pair can then be collected to generate a current. Basically, three generations of solar cells have already been realized:

- In the first generation, Si is used as an absorber. This indirect bandgap semiconductor requires thick layers to be efficient and at the present time, efficiency up to 24.4 % has been published in the literature [6];
- The second generation consists of a thin film as absorbing material with a bandgap fitting the solar spectrum. Several cells can be stacked in order to increase the total efficiency. A widely used candidate is CdTe because of its direct bandgap of 1.56 eV at room temperature and efficiency of 16.5 % has been reported for CdTe-based solar cells [7]. Note that the emission of heavy metals such as Cd was stated as pollutant generated by fossil fuel-based power plants but in the case of Cd used for the production of photovoltaic solar cells, the overall toxic emissions are 90 to 300 times lower.

  In thin films-based solar cells, the defect density has a strong influence on the efficiency of the solar cell. Indeed, they act as traps for the free electrons and holes and lead to the recombination of the electron-hole pair before its extraction from the semiconductor;
- The third generation is designed to decrease the loss of efficiency due to thermalization of the hot carrier when the photon energy is too high compared to the band gap. This can be done by using nanostructures as adsorbing material instead of thin films.

At the present time, the majority of the commercial solar cells emerged from the first and the second generations.

For CdTe-based solar cells, increasing the quality of the CdTe layer by decreasing the defect density is needed to optimize the working conditions of second generation solar cells. Moreover, this improvement can be implemented to another field of research based on CdTe: the infrared (IR) detection systems. Indeed, CdTe is also used as a substrate for the subsequent growth of IR detectors based on $Hg_xCd_{1-x}Te$ (MCT) where x is the mercury concentration. The advantage of this ternary compound is that by adjusting the x fraction, it is possible to tune the bandgap. Such detectors working in a wide range of the IR spectrum have already been produced.

Both for its use as a solar cell or as a substrate for MCT, two conditions are required to achieve optimal efficiency of the device based on CdTe:

- Very pure and highly crystalline semiconductor;
- Compatibility with the modern read out electronic circuits (mostly silicon-based).

A widely used growth technique producing semiconductors with the required cristallinity and with an accurate control of the elements constituting the semiconductor compound is molecular beam epitaxy (MBE). This technique was developed by A.Y. Cho and J.R. Arthur in 1969 [8]. The advantages of this growth process are that it allows the control of the fraction of each evaporated element (crucial point for the fabrication of MCT tunable detectors) and insures a very low concentration of impurities. Moreover, in comparison with other growth techniques, the semiconductor layers are grown at low temperature, leading to sharp interfaces between layers of different composition due to negligible diffusion. CdTe has already been grown by MBE on several substrates such as Ge [9], InSb or GaAs [10] but the best candidate to ensure easy compatibility with the read-out circuitry is probably Si [11]. Numerous advantages can be found in using Si as a substrate for CdTe:

- The growth technology of Si wafers is perfectly controlled so that the cristallinity of the silicon substrate is close to perfection: the surface is nearly defect and contaminant free and the doping of the substrate can be accurately controlled;
- The cost of the substrate is low compared to other materials because silicon is widely used for years now in modern electronic circuits;
- Read out circuitry is Si-based.

However, some challenges have to be considered for the growth of the CdTe film on Si:

- A huge lattice mismatch between the two compounds (19%), leading to a critical thickness close to zero and the creation of dislocations to relax the strain;
- A difference between the thermal expansion coefficients of CdTe and Si of 110% (respectively 4.8 10^{-6} and 2.3 10^{-6} K^{-1}). This can cause cracks or peeling of the epilayer and can generate defects during thermal cycles.

Regarding the absorber material, the limitations in the efficiency of photovoltaic cells and IR detectors are correlated to the defect density and the matching between the semiconductor bandgap and the energy of the photon to be detected. These defects arise mainly from the lattice mismatch between CdTe and Si: dislocations appear to relax the epilayer. A recent

theory predicts that new relaxation mechanisms should appear if the growth is performed selectively on nanoscale seeds instead of bi-dimensional surfaces [12, 13]. This should decrease the defect density and hence improve the yield of CdTe based devices. The concern is to check if it is possible to grow selectively on the seeds with no growth on the substrate in between.

The aim of this thesis is to obtain and to explain the selective growth of CdTe by MBE. Two kinds of patterned substrates are used for this study: CdTe(211)B seeds on naturally oxidized Si(211) and Si(100) seeds on SiO_2.

The thesis is organised as follows. The next chapter reminds the physical properties of Si, CdTe and ZnTe and basics of structural crystallography both in the real and the reciprocal spaces. This is necessary to explain the experimental results obtained by diffraction. Chapter III deals with the experimental techniques used to characterize the preparation of the samples and the selective growth process. These involve diffraction techniques (XRD, LEED and RHEED), spectroscopy and microscopy techniques (AES and PEEM) and MBE growth. The present state of the art for the growth of CdTe over the last decades is presented in the fourth chapter. Chapter V is the key stone and contains the experimental results about CdTe growth and selective growth of CdTe on CdTe or Si seeds patterned on SiO_2. At the end of this chapter, a selective growth mechanism is presented, based on the difference in the physisorption energies of CdTe on different substrates. A brief conclusion collecting the main results and discussions is presented along with perspectives in the last chapter.